Microstructure of sodium tripolyphosphate obtained by spry-kiln method

Marcin BANACH, Zygmunt KOWALSKI, Agnieszka MAKARA – Institute of Inorganic Chemistry and Technology, Cracow University of Technology, Cracow

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Introduction

Condensed phosphates are classified as inorganic polymers. There are three types of condensed phosphates: polyphosphates, cyclophosphates and ultraphosphates. Polyphosphates have a chain structure, ultraphosphates have a crosslinked structure. The degree of polymerisation ranges from 2 to 106 [1÷3].

One of the most important condensed sodium phosphates that are manufactured is sodium tripolyphosphate (Na$_5$P$_3$O$_10$∙6H$_2$O, STPP). It has been manufactured in bulk quantities since 1940 and it is used as component for detergents. The reason for the widespread use of STPP in detergents is its advantageous properties: ability to sequester calcium and magnesium ions in hard water, buffering capabilities, emulsion stabilising capability, defloculating and dispersing properties [4,5].

Sodium tripolyphosphate (pentasodium triphosphate, STPP) exists in three crystalline forms. The stable form is the hexahydrate (Na$_5$P$_3$O$_10$∙6H$_2$O). The other two polymorphic forms are anhydrous salts known as Phase I (high-temperature) and Phase II (low-temperature) [6÷8].

Phase I is formed at above 450°C, Phase II is formed at up to about 400°C. Manufactured STPP usually contains both these phases.

The anion of sodium tripolyphosphate consists of three condensed phosphate tetrahedrons. The P-O bonds in the anion form a broken line. The structure of the anion of Phase I, in comparison to that of Phase II, is characterized by higher deformation of terminal PO$_4$ groups and reverse internal symmetry of the molecule [8÷10].

Both Phase I and Phase II crystallize in the monoclinic system. The principal difference between them is in the coordination of sodium ions [11÷13]. Two of the three independent sodium atoms in Phase I are coordinated by distorted oxygen tetrahedrons, with one of them positioned in the centre of inversion. The third sodium atom is surrounded by only four oxygen atoms.

In the crystallographic structure of Phase II, three sodium atoms are coordinated octahedrally by oxygen atoms.

Phase I, as compared to Phase II, is characterized by higher rate of hydration, which is the result of crystal structure distortion.

Sodium tripolyphosphate is manufactured commercially using either a one-step or a two-step method. Irrespective of the manufacturing method, sodium tripolyphosphate production comprises three chemical processes, and the production line includes Neutralization of caustic soda solution with phosphoric acid, condensation ofcondensates, and calcination products.

The mixture of sodium pyrophosphates (disodium dihydrogen pyrophosphate and tetrasodium pyrophosphate) condenses during calcination and forms pentasodium triphosphate (STPP):

\[ \text{Na}_2\text{H}_2\text{P}_2\text{O}_7 + 2\text{Na}_2\text{P}_2\text{O}_7 = 2\text{Na}_5\text{P}_3\text{O}_{10} + \text{H}_2\text{O} \]

Drying and calcination conditions have an impact on the physicochemical properties of the product. Calcination temperatures determine the weight ratio of Phase I to Phase II in the final product [8, 9, 14].

This paper presents the results of investigations on the production of sodium tripolyphosphate, its physicochemical properties and on the effect of temperature on the morphology of calcination products.

Experimental

The starting material used in the tests was a mixture of sodium phosphates obtained in the spray drying process in an industrial STPP manufacturing plant.

In order to obtain sodium tripolyphosphate, the mixture of sodium phosphates was calcined in a chamber kiln for 60 minutes at 350 to 550°C.

The phase composition of the starting material and of the products was determined by X-ray radiography using a Philips X'Pert diffractometer with a graphite monochromator PW 1752/00.

Thermal analyses of sodium phosphates was conducted on a SDT 2960 Simultaneous DTA-DTG thermal analyser from TA Instruments. Measurements were performed in air in the temperature range of 20÷800°C at a heating rate of 20°C/min.

Photographs of the grains were made using a Nikon Eclipse LV100 microscope. The material studied was also observed under a Hitachi S-4700 scanning electron microscope, which enabled the determination of material morphology. Samples were sputter-coated with Pd/Pt by means of a Cressington 208 HR sputter coater from Cressington Scientific Instruments Ltd.

Adsorption methods based on the plotting of gas adsorption/desorption isotherms were applied to determine specific surface area of the studied materials, pore volume and size distribution. Nitrogen adsorption/desorption measurements were made using ASAP 2405 apparatus from Micromeritics.

Density measurements were made using an AccuPyc 1330 helium pycnometer from Micromeritics. Bulk density was determined according to Polish standard PN-80/C-04532 [15]. Pycnometric density of pelletized material was determined in a glass pycnometer. Kerosene was used as the liquid of known density, inert to samples. When the densities of the porous materials were known, their total and open porosity could be determined.

Discussion of results

It was found, on the basis of X-ray analysis, that the basic crystalline phase of the starting material used was a double salt of monosodium and disodium orthophosphates (NaH$_2$PO$_4$·Na$_2$HPO$_4$). The phases accompanying the double salt were disodium orthophosphate...
(Na₃HPO₄), disodium orthophosphate dihydrate (Na₂HPO₄·2H₂O), sodium pyrophosphate (Na₅P₃O₁₀) and monosodium orthophosphate (NaH₂PO₄).

The result of thermal analysis of spray dried sodium phosphates, which enables determination of phase transitions that occur during the formation of sodium tripolyphosphate, is shown in Figure 1.

At ca. 73°C adsorbed water is released and Na₂HPO₄·2H₂O is decomposed.

Spray drying of the solution of sodium orthophosphates may lead to the formation of compounds of such disrupted structure, that they resemble amorphous substances. With increasing temperature during calcination (up to ca. 130°C) these compounds undergo recrystallisation.

In the temperature range of 180÷200°C monosodium phosphate is converted into disodium dihydrogen pyrophosphate (Na₂H₂P₂O₇). At the temperature of 200÷250°C Na₂P₂O₇ is formed. At about 200°C anhydrous Na₅P₃O₁₀ is also formed. During further heating its rate of formation increases and reaches a maximum at ca. 290°C. At temperatures of up to 450°C the condensate structure takes on its rate of formation increases and reaches a maximum at ca. 290°C. At temperatures of up to 450°C the condensate structure takes on its form. In the 450÷550°C range Phase II is transformed into Phase I.

Transformations observed in the 360÷410°C range are associated with the displacement of atoms due to diffusion in the solid body, leading to the synthesis of new compounds as the result of rearrangement of the starting material. At temperatures above 350°C low-molecular sodium metaphosphates (NaPO₃) start to form and are then transformed into higher molecular form (Na₅P₃O₁₀). The exothermal effect at ca. 480°C may be attributed to polymorphic transformation of the low-temperature phase of STPP into the high-temperature phase.

At temperatures of up to 500°C the starting material and the products determined by analysis of sorption isotherms. The table also includes the values of true density (dₜ), bulk density (dₑ) and pycnometric density (dₚ). These values were used to determine the relative density (dₑ/ₜ), total porosity (Pₒ) and open porosity (Pₖ) of the materials.

Table 1 Parameters of microstructure of the starting material used and of calcinations products determined on the basis of densimetric and nitrogen sorption measurements

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Starting material</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcination temperature (T)</td>
<td>°C</td>
<td>-</td>
<td>350</td>
</tr>
<tr>
<td>Bulk density (dₑ)</td>
<td>g/cm³</td>
<td>0.4053</td>
<td>0.4073</td>
</tr>
<tr>
<td>True density (dₜ)</td>
<td>g/cm³</td>
<td>2.4828</td>
<td>2.6307</td>
</tr>
<tr>
<td>Pycnometric density (dₚ)</td>
<td></td>
<td>1.2961</td>
<td>1.6354</td>
</tr>
<tr>
<td>Relative density (dₑ/ₜ)</td>
<td>%</td>
<td>16.32</td>
<td>15.48</td>
</tr>
<tr>
<td>Total porosity (Pₒ)</td>
<td>%</td>
<td>83.68</td>
<td>84.52</td>
</tr>
<tr>
<td>Open porosity (Pₖ)</td>
<td>%</td>
<td>68.73</td>
<td>75.09</td>
</tr>
<tr>
<td>Specific surface area (Sₘeṣo)</td>
<td>m²/g</td>
<td>0.99</td>
<td>0.63</td>
</tr>
<tr>
<td>External surface area (Sₑ)</td>
<td>m²/g</td>
<td>1.84</td>
<td>1.08</td>
</tr>
<tr>
<td>Mesopore surface area (Sₘₖo)</td>
<td>m²/g</td>
<td>1.17</td>
<td>0.76</td>
</tr>
<tr>
<td>Total pore volume (Vₜ)</td>
<td>cm³/g</td>
<td>0.0022</td>
<td>0.0017</td>
</tr>
<tr>
<td>Mesopore volume (Vₘeṣo)</td>
<td>cm³/g</td>
<td>0.0021</td>
<td>0.0017</td>
</tr>
<tr>
<td>Average pore diameter (Dₑ)</td>
<td>nm</td>
<td>7.01</td>
<td>6.83</td>
</tr>
<tr>
<td>Mesopore diameter (Dₘₖo)</td>
<td>nm</td>
<td>7.24</td>
<td>8.88</td>
</tr>
</tbody>
</table>

Table 1 lists the texture properties of the particles of the starting material and of the products determined by analysis of sorption isotherms. The table also includes the values of true density (dₜ), bulk density (dₑ) and pycnometric density (dₚ). These values were used to determine the relative density (dₑ/ₜ), total porosity (Pₒ) and open porosity (Pₖ) of the materials.

Figure 2 shows microscopic images of particles of the starting material and of product examples. Figure 3 shows a SEM microphotographs of tested samples. The function of pore volume distribution vs. linear pore size is shown in Figure 4.

The high total porosity of sodium phosphates (Pₒ = 83.68%), which translates into their low bulk density, is the result of specific morphology of particles. The grains of sodium phosphates have a spherical shape and characteristic “hollow shell” structure with wrinkled surface (Fig. 2). The examination of micro areas of the material shows that it is not uniform (grains vary in size and shape). The spray dried mixture has a form of polycrystalline aggregates. Diverse sizes and shapes also feature pores formed between the grains.
Calcination preserves the structure of the starting material used. The presented microphotographs of STPP display the spherical structure of particles being the result of preserving the “hollow shell” structure of sodium phosphates after spray drying (Fig. 2). This is also confirmed by the high total and open porosities of this material (ca. 84% and 75%, respectively). The total and open porosities of the starting material are 84% and 70%, respectively.

Comparison of the images of the powder obtained at 350°C and those of sodium phosphate starting material (Fig. 3), indicates change of shape and size of the grains. The grains become partly more rounded and larger. The surface of contact between the grains also increases.

The result of microstructure changes is the decreasing of the specific surface area: from 0.99 m²/g of the sodium phosphates to 0.63 m²/g of sodium tripolyphosphate obtained at 350°C (Tab.1). The pore volumes and sizes are also contracted.

Material calcined at 400°C shows transitional loosening of the packing of grains and increased grain size. Pore volume distribution curves (Fig. 4) indicate substantial increase in mesoporosity. The logarithmic curve also indicates higher abundance of macropores. These changes cause increase in the development of the specific surface area of the material.

Specific in the microstructure of STPP obtained by calcination in 450°C and 500°C is the presence of oval and fibrous grains. Increased packing of grains, increased contact surface between grains and increased grain size are observed in the microstructure of material at 450°C and 500°C. The number and size of pores decrease, and the grains gradually form the solid skeleton of the material.

Sodium tripolyphosphate obtained at 550°C contains monocrystalline grains with highly developed flat walls formed during liquid phase solidification. At this temperature of calcination the solid phase is partially transformed into liquid phase, which then resolidifies. The solidification of the liquid phase eliminates the smallest pores and decreases specific surface area. At the same time the process leads to the formation of a large number of macropores.

Conclusions

The phase composition of products depends on the calcination temperature. At 350−450°C Phase II STPP is obtained, at 500°C a mixture of Phase II and Phase I, and at 550°C Phase I only.

The temperature of calcination also has an effect on the microstructure of sodium tripolyphosphate. At 350−500°C the grains become more rounded and larger. After calcination at 550°C the grains have a fibrous form, the volume of the pores and the free surface area are increased. The change in morphology is the result of the presence of liquid phase at temperatures above 500°C. The liquid phase, present in the form of layers between solid grains, melts the grains. When the saturation concentration is exceeded, the solid phase reprecipitates from the liquid. This leads to decrease of pore volumes and denser packing of grains.
During the calcination of sodium phosphates the point of contacts between the grains are transformed into phase contacts with a higher surface development. Mass transfer within the porous set of grains into void spaces causes growth of grains and transformation of that set of grains into a solid polycrystal. Another effect of mass transfer is decrease of the free surface development and transformation thereof into grain boundaries. Small pores inside the spaces of dense grain arrangement are eliminated more rapidly than the wide pores between agglomerates. The result is breaking up of contacts between the grains, growth of pores and increased volumetric share of pores between agglomerates, and in consequence non-uniform microstructure. The processes of mass transfer are accompanied by a number of other phenomena, such as reactions between components or phase transitions, which can cause transitional changes in the microstructure.

**Literature**

15. PN-80/C-04532. Oznaczanie gęstości nasypowej.

Marcin BANACH - Ph.D., (Eng), graduated from the Faculty of Chemical Engineering and Technology of the Cracow University of Technology (2006). He is currently an Assistant Professor at the CUT. Specialisation – inorganic chemical technology. e-mail: marcinbanach@chemia.pk.edu.pl

Zygmunt KOWALSKI - Professor (Ph.D., Eng), graduated from the Faculty of Mathematics, Physics and Chemistry of the Jagiellonian University (1996). He is currently Head of Inorganic Technology and Environmental Biotechnology Chair and the dean of the Faculty of Chemical Engineering and Technology of the Cracow University of Technology. Specialisation – inorganic technology and environmental protection

Agnieszka MAKARA - M.Sc., graduated from the Faculty of Chemical Engineering and Technology of the Cracow University of Technology (2007). Doctoral student of the Department of Inorganic Technology and Environmental Biotechnology of that University. Specializes in inorganic chemical technology.

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Everybody can suggest an own product, service or development, or nominate their favourite example from another organisation. The organizers clearly encourage the global bioplastics community to participate. However, the winning company must send a representative to Berlin, Germany on 22/23 Nov. 2011 to receive the award. Details about the award can be found at www.bioplasticsmagazine.de/award. The entry should state: 1. Name and details of the company or person that should win the award. What the product, service or development is and does. 3. Why you think this product, service or development should win an award. What your (or the proposed) company or organisation does. Each entry should not exceed 500 words (approx one page) and may also be supported with photographs, samples, marketing brochures and/ or technical documentation. Completed entries shall be sent to award@bioplasticsmagazine.com. Winners will be announced on 22/23 Nov. 2011 during the 6th European Bioplastics Conference and published in the December issue of bioplastics MAGAZINE.

Selection of the winner will be made by a panel of independent judges from Europe, America and Asia assembled by bioplastics MAGAZINE. The decision of the judging panel is final and binding. A pdf form for an award proposal can be found at www.bioplasticsmagazine.de/award (http://www.naukawpolsce.pap.pl/6.09.2011)